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Spectroscopic investigation of the dynamical behavior of the photoinduced phase transition of $\text{Na}_{0.6}\text{Co}_{1.3}[\text{Fe}(\text{CN})_6]\cdot 4\text{H}_2\text{O}$

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The dynamics of the photoinduced phase transition (PIPT) has been investigated for the Co-Fe cyanides film, $\text{Na}_{0.6}\text{Co}_{1.3}[\text{Fe}(\text{CN})_6]\cdot 4\text{H}_2\text{O}$, by means of the transient absorption spectroscopy. At low temperatures (≤ 150 K), the compound shows the permanent PIPT from the low-spin phase [LS phase: $\text{LS Co}^{3+} (t_{2g}^3 t_{2g}^3) - \text{LS Fe}^{2+} (t_{2g}^3 t_{2g}^3)$] to the high-spin phase [HS phase: $\text{HS Co}^{2+} (t_{2g}^3 t_{2g}^2 e_{g\uparrow}^2) - \text{LS Fe}^{3+} (t_{2g}^3 t_{2g}^2)$]. We have found that the film shows the transient PIPT into the HS phase above ~ 170 K, and the lifetime τ_{PI} of the photoinduced phase exponentially decreased from 10 ms at 170 K to ~ 100 μs at 260 K. In the early stage ($\Delta t \leq 200$ ns) of the PIPT, we further have observed a characteristic photoinduced absorption band (Y band) and ascribed the band to the $\text{LS Co}^{2+} (t_{2g}^3 t_{2g}^3 e_{g\uparrow}^1)$ state.

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I. INTRODUCTION

The photoinduced phenomena¹ have been extensively investigated both from the fundamental and technical points of view. In an extreme case, the photoexcitation causes the macroscopic structural change, or the so-called photoinduced phase transition (PIPT). Thus far, a long list of researchers reported the *persistent* PIPTs in spin-crossover complexes,^{2–5} transition metal cyanides,^{6–11} mixed-valence gold complex, $\text{Cs}_2\text{Au}_2\text{Br}_6$,¹² iodine-bridged binuclear Pt compounds,¹³ organic radical crystal, TTTA (1,3,5-trithia-2,4,6-triazapentalenyl),¹⁴ polydiacetylene crystal,¹⁵ and so on. In these systems, the photoinduced lattice structure is permanently maintained after the photoexcitation stops. On the other hand, Collet *et al.*¹⁶ have performed a time-resolved x-ray-diffraction measurement in organic charge-transfer salts, TTF-CA (tetrathiafulvalene-*p*-chloranil). They observed a *transient* PIPT phenomenon: the photoinduced phase transition from the neutral phase to ionic phase completed in 0.5 ns, but the photoinduced (PI) phase is not metastable and recovers to the ground state (neutral phase) within 1 ms. Here, we stress that the repetition behavior of the transient PIPT is quite important because it enables us to investigate the dynamical behavior by means of the transient absorption spectroscopy.

Among the photosensitive materials, the Co-Fe cyanides, whose chemical formula is $\text{A}_x\text{Co}[\text{Fe}(\text{CN})_6]_y \cdot z\text{H}_2\text{O}$ ($\text{A} = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$), have been attracting renewed interest of material scientists because they show a photoinduced magnetization^{6,7} as well as photoinduced structural change.¹⁰ For example, Sato *et al.*⁶ reported enhancement of magnetization in $\text{K}_{0.14}\text{Co}[\text{Fe}(\text{CN})_6]_{0.71} \cdot 4.93\text{H}_2\text{O}$ by irradiation of a red light (660 nm) at 5 K and suppression of magnetization by irradiation of a blue light (450 nm) at 5 K. In addition, a

thin films of Co-Fe cyanide, which is indispensable for a reliable transient absorption spectroscopy, can be grown on a SnO_2 -coated glass by the electrochemical reduction technique.^{18–20} Thus, we have chosen the Co-Fe cyanide as a target material for the detailed investigation on the dynamical behavior of the PIPT.

Crystallographically, the Co-Fe cyanides belong to the fcc group ($Fm\bar{3}m$; $Z=4$), in which Co and Fe ions form a rock-salt-type (NaCl-type) network with sharing cyano (CN^-) moieties.²¹ Parts of the $\text{Fe}(\text{CN})_6$ sites, however, are vacant and are replaced by six waters (H_2O). Most of the Co-Fe cyanides show a first-order phase transition from the low-spin (LS) phase [LS phase: $\text{LS Co}^{3+} (t_{2g}^3 t_{2g}^3) - \text{LS Fe}^{2+} (t_{2g}^3 t_{2g}^3)$] to the high-spin (HS) phase (HS phase: $\text{HS Co}^{2+} (t_{2g}^3 t_{2g}^2 e_{g\uparrow}^2) - \text{LS Fe}^{3+} (t_{2g}^3 t_{2g}^2)$) as temperature increases. This thermally induced phase transition accompanies a significant increase of the lattice constant a from ≈ 9.9 Å in the LS phase to ≈ 10.3 Å in the HS phase. At low temperatures (≤ 150 K), a similar phase transition from the LS phase to the HS phase is induced by photoexcitation,^{10,11} which forcibly transfers an electron from the LS Fe^{2+} site to the LS Co^{3+} site. Then, the photo-induced magnetism^{6,7} is rationally ascribed to the persistent PIPT from the (nonmagnetic) LS phase to the HS phase. The PI phase, however, *melts* into the LS phase as temperature increases above ~ 150 K.

In this paper, we have investigated the dynamical behavior of the PIPT of the Co-Fe cyanides film, $\text{Na}_{0.6}\text{Co}_{1.3}[\text{Fe}(\text{CN})_6]\cdot 4\text{H}_2\text{O}$, by means of the transient absorption spectroscopy. At high temperatures, we observed a broad absorption band located at ~ 2.4 eV, indicating the transient PIPT into the HS phase. The lifetime τ_{PI} of the PI phase exponentially decreases from 10 ms at 170 K to ~ 100 μs at 260 K. In the early stage ($\Delta t \leq 120$ ns) of the PIPT, we further have observed a characteristic photoinduced

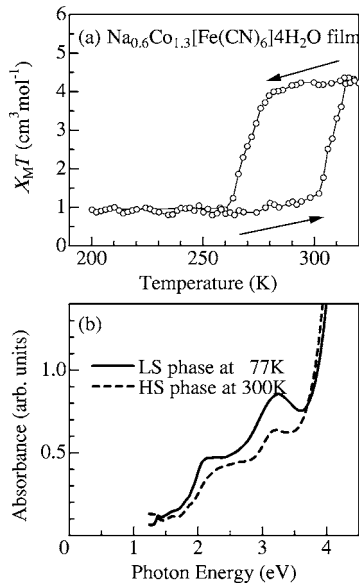


FIG. 1. (a) Temperature dependence of $\chi_M T$ of $\text{Na}_{0.6}\text{Co}_{1.3}[\text{Fe}(\text{CN})_6]\cdot 4\text{H}_2\text{O}$, where χ_M is the magnetic susceptibility. (b) Absorption spectra at 77 K in the LS phase (solid curve) and at 300 K in the HS phase (broken curve).

absorption band (Y band) at ≈ 1.7 eV, and ascribed the band to the LS Co^{2+} ($t_{2g}^3 e_g^1$) state.

II. EXPERIMENTAL

A. Sample preparation and characterization

The Co-Fe cyanide film was prepared on a SnO_2 -coated glass according to the procedure described elsewhere.¹⁸ With use of a superconducting quantum interference device (SQUID) magnetometer, we have measured temperature dependence of the magnetic susceptibility χ_M of the film. Figure 1(a) shows temperature dependence of $\chi_M T$ of the film, which is a crude measure for the effective spin moment. As seen in Fig. 1(a), the film shows the LS-to-HS transition at $T_{c\uparrow}=306$ K in the warming run, and at $T_{c\downarrow}=268$ K in the cooling run. Based on the thusly determined transition temperatures,²² the chemical composition of the film was estimated at $\text{Na}_{0.6}\text{Co}_{1.3}[\text{Fe}(\text{CN})_6]\cdot 4\text{H}_2\text{O}$.

We show, in Fig. 1(b), absorption spectra of the Co-Fe cyanide film at 77 K in the LS phase and at 300 K in the HS phase. In both the phases, two characteristic peak structures are observed below ~ 3.5 eV. The LS-HS phase transition significantly modifies the absorption spectrum in the visible region because of the concomitant cooperative charge transfer from the Fe^{2+} site to the Co^{3+} site. Figure 2 shows the magnified absorption spectra in the visible region. The spectrum indicated by broken curve stands for the photoinduced (PI) phase at 80 K, which was measured after photoexcitation by a halogen lamp for several minutes. The photoexcitation suppresses the absorption in the energy region of 2–3 eV. The spectral profile of the PI phase (broken curve) resembles with that at 300 K in the HS phase (thin solid curve¹⁷), indicating that PI phase has the same electronic configuration as the HS phase.¹⁸

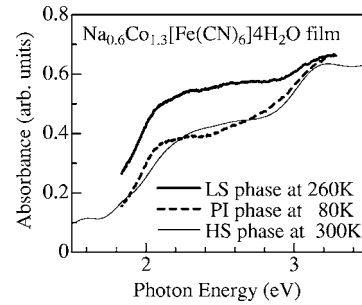


FIG. 2. Magnified absorption spectra of $\text{Na}_{0.6}\text{Co}_{1.3}[\text{Fe}(\text{CN})_6]\cdot 4\text{H}_2\text{O}$ at 260 K in the LS phase (solid curve) and at 300 K in the HS phase (thin solid curve). A broken curve stands for the PI phase at 80 K.

B. Time-resolved absorption spectroscopy

We used a nanosecond optical parametric oscillator (OPO) system pumped by a YAG laser (355 nm, 10 Hz) as an excitation source. The pulse width was 3–5 ns. For the time-resolved spectroscopy, light from a halogen lamp was focused on the sample film and the transmitted light was detected with a gated charge-coupled device (CCD) camera attached at the output stage of a grating monochromator. In the measurement of the small Δt spectra, we put a polarizer in front of the monochromator in order to eliminate the intense scattering from the excitation light. The time resolution of the system was 12 ns.

In order to obtain the overall temporal behavior of the photoinduced absorption change, we used continuous-wave lasers, e.g., He-Ne laser (1.85 eV) and yttrium aluminum garnet (YAG) laser (2.33 eV), as a probe light source. The intensity change $T_{1.85 \text{ eV}}$ ($T_{2.33 \text{ eV}}$) of the transmitted light was detected with a P-intrinsic-N (PIN) photodiode, and the temporal behavior of $T_{1.85 \text{ eV}}$ ($T_{2.33 \text{ eV}}$) was accumulated with a digital oscilloscope.

III. RESULTS AND DISCUSSION

A. Transient photoinduced phase transition

Figure 3(a) shows the differential absorption spectra of $\text{Na}_{0.6}\text{Co}_{1.3}[\text{Fe}(\text{CN})_6]\cdot 4\text{H}_2\text{O}$ at 260 K. At $\Delta t=500$ ns, the photoexcitation significantly suppresses the absorption in the energy region of 2–3 eV. The magnitude of the differential absorption decreases as the delay time Δt increases, and eventually, the signal disappears at $\Delta t=500 \mu\text{s}$. The lower panel of Fig. 3 shows the differential absorption spectra of the PI phase at 80 K, which was measured after photoexcitation by a halogen lamp for several min.. The profile of the transient absorption spectra [Fig. 3(a)] resembles that of the PI phase [Fig. 3(b)]. This clearly indicates that the photoexcitation on the Fe-Co cyanide film *transiently* creates the HS phase.

Figure 4 shows temporal behavior of the magnitude of the transient absorption at 260 K. The vertical axis (mass fraction ϕ) was normalized by the area of the differential absorption spectra of the PI phase. [see Fig. 3(b)] A broken curve is the best-fitted result with a exponential function, ϕ

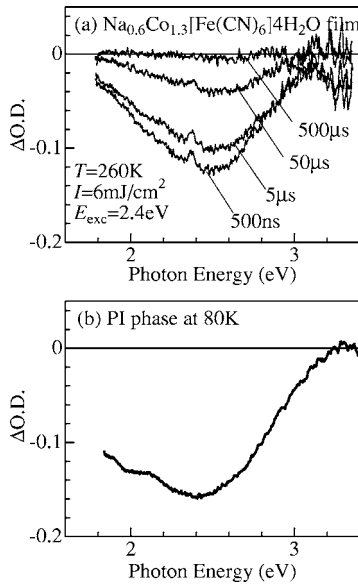


FIG. 3. (a) Differential absorption spectra of $\text{Na}_{0.6}\text{Co}_{1.3}[\text{Fe}(\text{CN})_6]\cdot 4\text{H}_2\text{O}$ at 260 K. The pulse energy and photon energy of the excitation light were $6 \text{ mJ}/\text{cm}^2$ and 2.4 eV , respectively. (b) Differential absorption spectra of the PI phase at 80 K, which was measured after photoexcitation by a halogen lamp for several minutes.

$=\phi_0 \exp[-(\Delta t/\tau)]$. The PI HS phase relaxes into the LS ground state with the lifetime τ_{PI} of $50 \mu\text{s}$.²³

The initial mass fraction ϕ_0 of the PI phase shows a notable photon energy dependence, as shown in Fig. 5. The excitation spectrum (open circles) shows a broad maximum at $\approx 2.4 \text{ eV}$, and does not trace the absorption spectra of the LS phase (solid curve). This spectral difference between the excitation and absorption spectrums clearly excludes the conventional heating effect as an origin for the observed transient PITP phenomenon. The peak position of the excitation spectrum roughly coincides with first peak of the absorption spectrum. Based on the *ab initio* cluster calculation, Kawamoto *et al.*²⁴ assigned the first absorption peak to the dipole-allowed charge-transfer excitation from the LS Fe^{2+} ($t_{2g}^3 t_{eg}^3$) site to the LS Co^{3+} ($t_{2g}^3 t_{eg}^3$) site. Then, the excita-

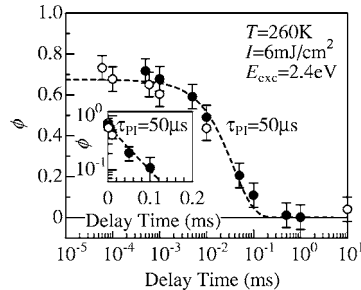


FIG. 4. Mass fraction ϕ of the PI phase of $\text{Na}_{0.6}\text{Co}_{1.3}[\text{Fe}(\text{CN})_6]\cdot 4\text{H}_2\text{O}$ at 260 K. The pulse energy and photon energy of the excitation light were $6 \text{ mJ}/\text{cm}^2$ and 2.4 eV , respectively. A broken curve is the best-fitted result with a exponential function, $\phi = \phi_0 \exp[-(\Delta t/\tau)]$. Open and filled circles were the data obtained at the different runs. Inset shows a single logarithm plot of ϕ against Δt .

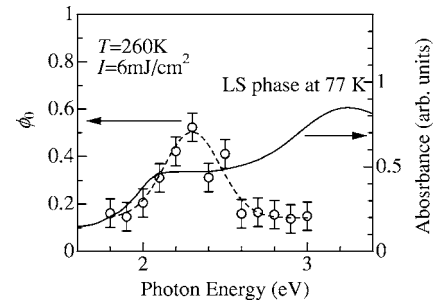


FIG. 5. Photon energy dependence of the initial mass fraction ϕ_0 ($\Delta t = 500 \text{ ns}$) of the PI phase of $\text{Na}_{0.6}\text{Co}_{1.3}[\text{Fe}(\text{CN})_6]\cdot 4\text{H}_2\text{O}$ at 260 K. A solid curve represents the absorption spectrum of the LS phase at 77 K. The excitation energy was adjusted to $6 \text{ mJ}/\text{cm}^2$. A broken curve is merely a guide to the eyes.

tion spectrum suggests that the initial charge-transfer plays significant role in the PIPT of the Co-Fe cyanide. Here, we stress that the LS Co^{3+} site is transferred to the LS Co^{2+} ($t_{2g}^3 t_{eg}^1$) state immediately after the photoexcitation. In order to complete the PIPT into the HS phase, however, the intersystem crossing from the LS Co^{2+} ($t_{2g}^3 t_{eg}^1$) to the HS Co^{2+} ($t_{2g}^3 t_{eg}^2$) is indispensable.

We show in Fig. 6(a) temperature dependence of the lifetime τ_{PI} of the PI phase. These values were estimated by the least-squares fitting of the $\Delta T_{2.33} \text{ eV} - \Delta t$ curve as $\Delta T_{2.33} \text{ eV} = A \exp[-(\Delta t/\tau_{\text{PI}})]$. As shown by the straight line in Fig. 6(a), the lifetime τ_{PI} of the PI phase obeys a thermal-activation law; $\tau_{\text{PI}} \propto \exp(\Delta/T)$, where Δ ($\approx 0.23 \text{ eV}$) is the activation energy. It may be interesting that the magnitude of Δ is the same order as the transition entropy ΔH ($\approx 0.17 \text{ eV}$) of an analogous system $\text{RbMn}[\text{Fe}(\text{CN})_6]$.²⁵ The magnitude of ϕ_0 slightly increases with temperature. This is

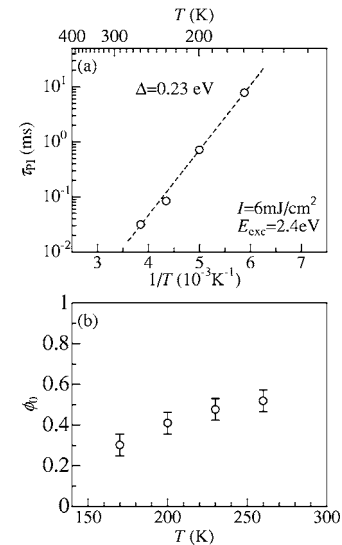


FIG. 6. Temperature dependence of (a) the lifetime τ_{PI} and (b) the initial mass fraction ϕ_0 (extrapolation) of the PI phase of $\text{Na}_{0.6}\text{Co}_{1.3}[\text{Fe}(\text{CN})_6]\cdot 4\text{H}_2\text{O}$ at 260 K. The pulse energy and photon energy of the excitation light were $6 \text{ mJ}/\text{cm}^2$ and 2.4 eV , respectively. A broken curve in (a) is the best-fitted result with a exponential function.

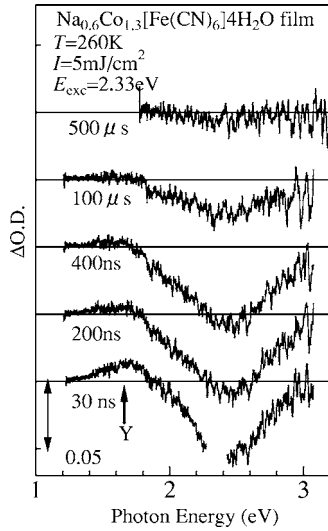


FIG. 7. Differential absorption spectra of $\text{Na}_{0.6}\text{Co}_{1.3}[\text{Fe}(\text{CN})_6]\cdot 4\text{H}_2\text{O}$ at 260 K. The pulse energy and photon energy of the excitation light were $5 \text{ mJ}/\text{cm}^2$ and 2.33 eV , respectively. An upward arrow indicates a photoinduced absorption band (Y band).

probably because the free energy of the PI phase approaches to that of the LS ground state as temperature increases. The reduced energy difference should enhance the quantum yield of the PIPT, even though the lifetime of the PI phase shortens with temperature.

B. Initial stage of the photoinduced phase transition

Now, let us proceed to the initial stage of the transient PIPT of the Co-Fe cyanide film. Figure 7 shows the differential absorption spectra of $\text{Na}_{0.6}\text{Co}_{1.3}[\text{Fe}(\text{CN})_6]\cdot 4\text{H}_2\text{O}$ at 260 K. At $\Delta t = 30 \text{ ns}$ (the lowest spectrum), we observed a photoinduced absorption band at $\approx 1.7 \text{ eV}$, as indicated by an upward arrow. Hereafter, we will call the absorption band “Y band.” The Y band is observed only in the early state after the photoexcitation and almost disappears at $\Delta t = 200 \text{ ns}$.

In order to derive the precise temporal behavior of the Y band, we decomposed the spectra into two Gauss components,

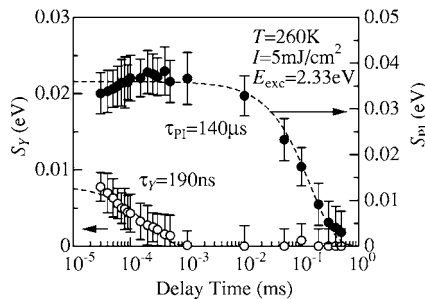


FIG. 8. Temporal behavior of the spectral weights of $\text{Na}_{0.6}\text{Co}_{1.3}[\text{Fe}(\text{CN})_6]\cdot 4\text{H}_2\text{O}$ at 260 K. Open circles represent the spectral weight S_Y of the Y band, whereas the filled circles does the spectral weight S_{PI} of the band due to the PI phase. Broken curves are the best-fitted result with exponential functions.

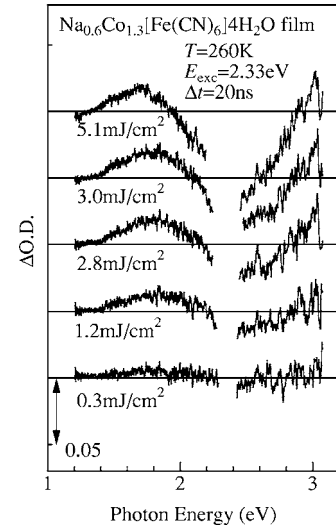


FIG. 9. Pulse energy dependence of differential absorption spectra of $\text{Na}_{0.6}\text{Co}_{1.3}[\text{Fe}(\text{CN})_6]\cdot 4\text{H}_2\text{O}$ at 260 K. The delay time Δt was set at 20 ns . The photon energy of the excitation light was 2.33 eV .

$$\Delta \text{O.D.} = \frac{S_Y}{\sqrt{2\pi}} \exp \left[-\frac{(\hbar\omega_Y - \hbar\omega)^2}{2\Gamma_Y^2} \right] - \frac{S_{\text{PI}}}{\sqrt{2\pi}} \exp \left[-\frac{(\hbar\omega_{\text{PI}} - \hbar\omega)^2}{2\Gamma_{\text{PI}}^2} \right], \quad (1)$$

where the spectral weight, S_Y and S_{PI} , stand for the Y band and the band due to the PI phase. Overall spectral profile was adjusted by the two parameters, S_Y and S_{PI} , and the other parameters are fixed as $\hbar\omega_Y = 1.75 \text{ eV}$, $\hbar\omega_{\text{PI}} = 2.45 \text{ eV}$, $\Gamma_Y = 0.62 \text{ eV}$, and $\Gamma_{\text{PI}} = 0.77 \text{ eV}$. We show in Fig. 8 the temporal behavior of the spectral weights of the Y band (open circles) and the band (filled circles) due to the PI phase. Broken curves are the best-fitted result with exponential functions. The lifetime τ_Y of the Y band is 190 ns , which is much faster than the lifetime $\tau_{\text{PI}} (=140 \mu\text{s})$ of the PI phase.

Figure 9 shows pulse energy dependence of the differential absorption spectra at 260 K. We also decomposed the spectra into two Gauss components (see Eq. (1)) and plotted the results in Fig. 10. The magnitude of S_Y linearly increases

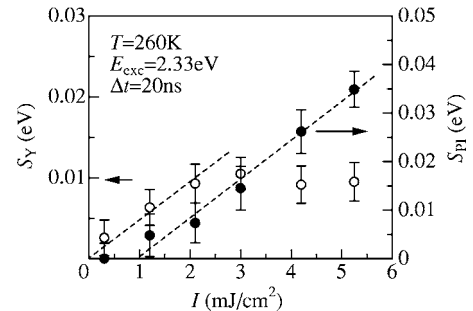


FIG. 10. Excitation energy (I) dependence of the spectral weights of $\text{Na}_{0.6}\text{Co}_{1.3}[\text{Fe}(\text{CN})_6]\cdot 4\text{H}_2\text{O}$ at 260 K. Open circles represent the spectral weight S_Y of the Y band, whereas the filled circles represent the spectral weight S_{PI} of the band due to the PI phase. Broken lines are merely a guide to the eyes.

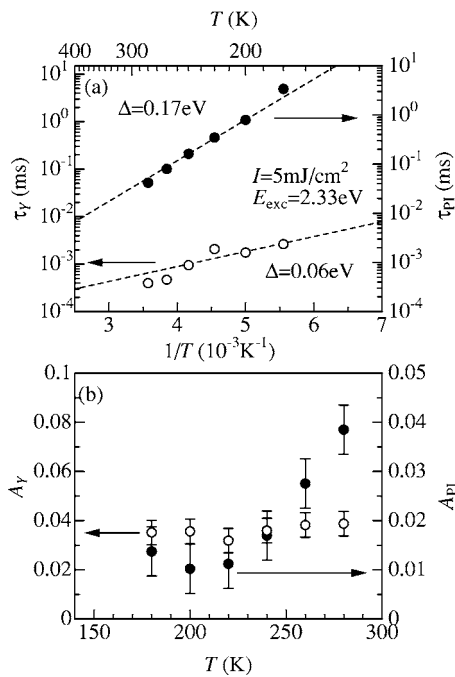


FIG. 11. Temperature dependence of (a) the lifetimes, τ_Y and τ_{PI} , and (b) the amplitudes, A_Y and A_{PI} . Open and filled circles are for the Y band and the band due to the PI phase, respectively. A broken curve in (a) are the best-fitted result with exponential functions. The pulse energy and photon energy of the excitation light were 5 mJ/cm² and 2.33 eV, respectively.

as I increase in the weak excitation region (see the broken line) and then is saturated when I exceeds ~ 2 mJ/cm². On the other hand, the magnitude of S_{PI} is rather suppressed in the weak excitation region, but steeply increases when I exceeds ~ 2 mJ/cm². Such a nonlinear (or threshold) behavior is frequently observed in the permanent PIPTs.^{8,12–15}

In order to investigate the temperature-dependent behavior, we first measured the $\Delta T_{1.85 \text{ eV}} - \Delta t$ curve as a function of temperature. The obtained $\Delta T_{1.85 \text{ eV}} - \Delta t$ curves were analyzed by two exponential functions

$$\Delta T_{1.85 \text{ eV}} = A_Y \exp\left(-\frac{\Delta t}{\tau_Y}\right) - A_{PI} \exp\left(-\frac{\Delta t}{\tau_{PI}}\right). \quad (2)$$

The former and the latter terms correspond to the Y band and the band due to the PI phase, respectively. The best-fitted results are shown in Fig. 11: (a) the lifetimes, τ_Y and τ_{PI} , and (b) the amplitudes, A_Y and A_{PI} . The lifetime τ_Y [open circles

in Fig. 11(a)] of the Y band show rather gradual temperature dependence, as compared to τ_{PI} (filled circles). The activation energy Δ (≈ 0.06 eV) of τ_Y is much smaller than that (≈ 0.17 eV) of τ_{PI} . On the other hand, amplitude A_Y [open circles in Fig. 11(b)] of the Y band is nearly independent of temperature, being in a sharp contrast to A_{PI} (filled circles).

Now, let us discuss the origin for the Y band. The Y band has the following characteristics: (1) the lifetime τ_Y exponentially increases as temperature decreases, (2) the signal intensity S_Y linearly increases with the excitation energy I , and (3) the amplitude A_Y is independent of temperature. These characteristics suggest that the Y band is due to some self-trapped excited state. The most plausible candidate for the state is the LS Co²⁺ state ($t_{2g\uparrow}^3 t_{2g\downarrow}^3 e_{g\uparrow}^1$), which is the intermediate state for the PIPT of the Co-Fe cyanide. The magnitude of τ_Y (~ 100 ns) is reasonable for such a state because the subsequent intersystem crossing into the HS Co²⁺ ($t_{2g\uparrow}^3 t_{2g\downarrow}^2 e_{g\uparrow}^2$) state would take a finite time. In addition, the transition energy (≈ 1.7 eV) of the Y band can be explained as follows. With the self-trapped LS Co²⁺ state, one may expect the additional $t_{2g\uparrow}^3 t_{2g\downarrow}^3 e_{g\uparrow}^1 - t_{2g\uparrow}^2 t_{2g\downarrow}^3 e_{g\uparrow}^2$ optical transition, whose transition energy is roughly the same as the ligand-field splitting of the [Co²⁺(NC)₆] complex. Then, the observed transition energy (≈ 1.7 eV) is reasonable, because the ligand-field splitting of the [Co²⁺(NC)₆] complex should be larger than that [≈ 1.04 eV (Ref. 26)] of the [Co²⁺(H₂O)₆] complex.

IV. SUMMARY

In summary, we have investigated the dynamical behavior of PIPT of the Co-Fe cyanide film, Na_{0.6}Co_{1.3}[Fe(CN)₆]·4H₂O, by means of the transient absorption spectroscopy. Based on the experimental observations, we have proposed the following process for the transient PIPT. First, the photoexcitation induces the charge transfer from the LS Fe²⁺ ($t_{2g\uparrow}^3 t_{2g\downarrow}^3$) site to the LS Co³⁺ ($t_{2g\uparrow}^3 t_{2g\downarrow}^3$) site. Immediately after the photoexcitation, the photo created LS Co²⁺ ($t_{2g\uparrow}^3 t_{2g\downarrow}^3 e_{g\uparrow}^1$) state causes the Y band, whose lifetime τ_Y is order of 100 ns. Then, the LS Co²⁺ state relaxes into the HS Co²⁺ ($t_{2g\uparrow}^3 t_{2g\downarrow}^2 e_{g\uparrow}^2$) via the intersystem crossing process to cause the macroscopic HS phase.

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